NBS TECHNICAL NOTE 928

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Computer Programs for the Evaluation of Activity and Osmotic Coefficients

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[2] Located at Boulder, Colorado 80302.

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Computer Programs for the Evaluation of Activity and Osmotic Coefficients

+ technical note, no. 928

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FOREWORD

The National Standard Reference Data System was established in 1963 for the purpose of promoting the critical evaluation and dissemination of numerical data of the physical sciences. The program is coordinated by the Office of Standard Reference Data of the National Bureau of Standards, but involves the efforts of many groups in universities, government laboratories, and private industry. The primary aim of the program is to provide compilations of critically evaluated physical and chemical property data. These tables are published in the *Journal of Physical and Chemical Reference Data,* in the NSRDS-NBS series of the National Bureau of Standards, and through other appropriate channels.

The task of critical evaluation involves careful analysis and comparison of data retrieved from the scientific literature. Computer programs are developed by NSRDS Data Centers when necessary to assist in this analysis. Such programs are made available when they are felt to be of value to the research community at large.

Further information on NSRDS and the publications which form the primary output of the program may be obtained by writing to the Office of Standard Reference Data, National Bureau of Standards, Washington, DC 20234.

David R. Lide, Jr., Chief
Office of Standard Reference Data

COMPUTER PROGRAMS FOR THE EVALUATION OF ACTIVITY AND OSMOTIC COEFFICIENTS

Bert R. Staples and Ralph L. Nuttall

ABSTRACT

A number of specialized computer programs have been developed for the purposes of calculating thermodynamic properties directly from experimental data and for subsequent data manipulation, including non-linear least-squares fitting of the data to empirical or semi-empirical equations that describe the function over a range of compositions, temperatures or other parameters. The details of the programs used in the critical evaluation of mean activity and osmotic coefficients and sample runs for each program are discussed. Osmotic coefficients can be calculated from direct vapor pressure measurements or from isopiestic molalities. Activity coefficients can be calculated from electromotive force measurements of galvanic cells, both without liquid-junction and with transference. A non-linear least-squares program fits data from all sources as a function of ϕ and $\ln \gamma$. Once the parameters of the fitting equation have been obtained, another program can be used to calculate a table of m, γ, ϕ, a_w, and ΔG^{ex} at rounded molalities.

Keywords: Activity coefficients; aqueous; computer programs; data evaluation; electrolytes; electromotive force; isopiestic method; non-linear least squares; osmotic coefficients; thermodynamic properties; vapor pressure.

1. Introduction

The Electrolyte Data Center at the National Bureau of Standards is engaged in the critical evaluation of equilibrium thermodynamic properties of electrolyte solutions. A number of specialized computer programs have been developed for the purposes of calculating thermodynamic properties from experimental data and for subsequent data manipulation, including non-linear least-squares fitting of the data to empirical or semi-empirical equations to describe the function over a range of compositions, temperatures or other parameters.

The computer programs form an essential part of the evaluation scheme. The documentation of the operations involved in such critical evaluations is desirable, in order to provide a set of tested programs suitable for the reduction of experimental data and as a ready reference for users of these programs.

This Technical Note presents the detailed equations involved in the critical evaluation of mean activity and osmotic coefficients and the details of programs which provide machine-calculation of these and related properties. The programs are listed in the Extended BASIC language and have been run on a time-shared CDC-6000 series system. In some cases data are obtained from stored on-line files.

The programs described in this Technical Note calculate values for the mean activity or osmotic coefficient from raw experimental data. The program 'VAPOR' calculates the osmotic coefficient, ϕ, from direct vapor pressure measurements while ϕ is calculated from isopiestic molalities by means of the program 'ISOPSTC'.

Activity coefficients, $\gamma_{\pm}$, are calculated from emf measurements of galvanic cells, both without liquid junction ('EMF') and with transference ('TRFNO').

A non-linear least-squares program, 'EVALU', fits data from all sources as a function of molality ϕ and ln $\gamma_{\pm}$. Once the parameters of the fitting equation have been obtained, another program, 'GAMPHI', can be used to calculate a table of m, $\gamma_{\pm}$, ϕ, a_w, and ΔG^{ex} at rounded molalities.

The most recent values of the fundamental constants [1][1] have been utilized throughout this Technical Note. Other constants refer to water at 298.15 K but are easily adapted to other temperatures or solvent systems.

---

[1] Figures in brackets indicate the literature references on page 48.

2. Fundamental Thermodynamic Relationships

Fundamental electrolyte thermodynamic relationships have been discussed in detail previously [2]. A summary is presented here.

The standard state is chosen such that the standard free energies of the dissociated and undissociated molecules are the same. Then the activity is given by

$$a_{salt} = a_2 = (a_+^{\nu+} a_-^{\nu-}) = a_\pm^{\nu} \qquad (1)$$

where

$$\nu = \nu_+ + \nu_- . \qquad (2)$$

Then

$$\mu_2 = \overset{\circ}{\mu_2} + \nu RT \ln a_\pm \qquad (3)$$

where

$$a_\pm = a_2^{1/\nu} = (m_+^{\nu+} m_-^{\nu-} \gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu} \qquad (4)$$

and taking a geometric mean of the ion activity coefficients

$$\gamma_\pm = (\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu} \qquad (5)$$

The mean ionic molality, $m_\pm$, is

$$m_\pm = m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \qquad (6)$$

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \qquad (7)$$

The properties of electrolytic solutions are, in general, directly related to the ionic strength of the solution, defined by:

$$I_m = 1/2 \sum_i z_i^2 m_i \qquad (8)$$

where z is the ionic charge number, and the subscript m designates I on the molality scale.

For a solution consisting of a single salt, $m_+ = \nu_+ m$ and $m_- = \nu_- m$, where m is the molality of the salt added. For such a solution of a pure salt, one then obtains

$$\gamma_\pm = \frac{a_\pm}{m(\nu_+^{\nu+} \nu_-^{\nu-})^{1/\nu}} \qquad (8)$$

3. Correlation of Experimental Data

To fit activity coefficient data over a range of composition the equation

$$\ln\gamma = \frac{-|z_+z_-|A_m I_m^{1/2}}{1 + B\ I_m^{1/2}} + Cm + Dm^2 + Em^3 + \ldots \tag{9}$$

is used to correlate the experimental data.

The parameters B, C, D, E, etc. are empirical [2]. The osmotic coefficient and excess Gibbs energy can be expressed in terms of the same parameters by

$$\phi = 1 + \frac{|z_+z_-|A_m}{B^3 I}\left[-(1 + B\ I^{1/2}) + 2\ \ln\ (1 + B\ I^{1/2}) + 1/(1 + B\ I^{1/2})\right] + \frac{1}{2}Cm + \frac{2}{3}Dm^2 + \frac{3}{4}Em^3 + ,\ldots\ . \tag{10}$$

and

$$\Delta G^{ex} = \nu mRT\left\{\frac{z_+z_-\ A_m}{B^3 I}\left[(2 - B\ I^{1/2})B\ I^{1/2} - 2\ \ln\ (1 + B\ I^{1/2})\right] + \frac{1}{2}cm + \frac{1}{3}Dm^2 + \frac{1}{4}Em^3 + \ldots\right\} \tag{11}$$

where I is used to represent I_m.

4. Types of Data Sources

Most determinations of activity and osmotic coefficients of an electrolyte solution are based on these experimental techniques:

(1) vapor pressure lowering

(2) Isopiestic or vapor pressure equilibration

(3) freezing point depression

(4) boiling point elevation

(5) electromotive forces (emfs) of galvanic cells without liquid junction

(6) emfs of galvanic cells with transference

(7) diffusion

The first four measure the activity of the solvent and the last three measure the activity of the solute.

5. Experimental Methods Measuring the Activity of the Solvent

5.1 Direct Vapor Pressure Measurements

Direct measurement of the vapor pressure over a solution is a method for determining the activity of the solvent. For the data using the pure solvent as reference, the solvent activity, a_1, and the osmotic coefficient of the salt, ϕ, can be calculated for each experimental point by

$$\ln a_1 = \ln(P/P_o) + \frac{B_T\ (P-P_0)}{RT} \qquad (12)$$

and

$$\phi = -\frac{1000}{\nu m M_1} \ \ln a_1 . \qquad (13)$$

where P is the pressure of the solvent vapor over the solution and P_o is that over pure solvent. For water at 25°C, we take P_o = 3168.6 Pa (23.766_5 Torr) [3], and B_T, the second virial coefficient for water vapor, $-992\ \text{cm}^3.\text{mol}^{-1}$ from the Steam Tables [4]. Corrections for non-ideality of water vapor are given by the second term on the right of eq (12).

The program "VAPOR" was designed to perform the calculation of the osmotic coefficients from data obtained from direct vapor pressure measurements.

5.1a. Program: VAPOR

General Description.

The program VAPOR, using the vapor pressure of the pure solvent, P_o, and the measured vapor pressure of the solution, P, calculates the activity of the solvent in the solution.

The osmotic coefficient is then calculated using eq (13). The procedure is presented diagramatically in figure 1.

The program listing is presented in list 1. Notations and explanatory statements are indicated in lines beginning with "REM" (remarks). A sample run is presented as list 2.

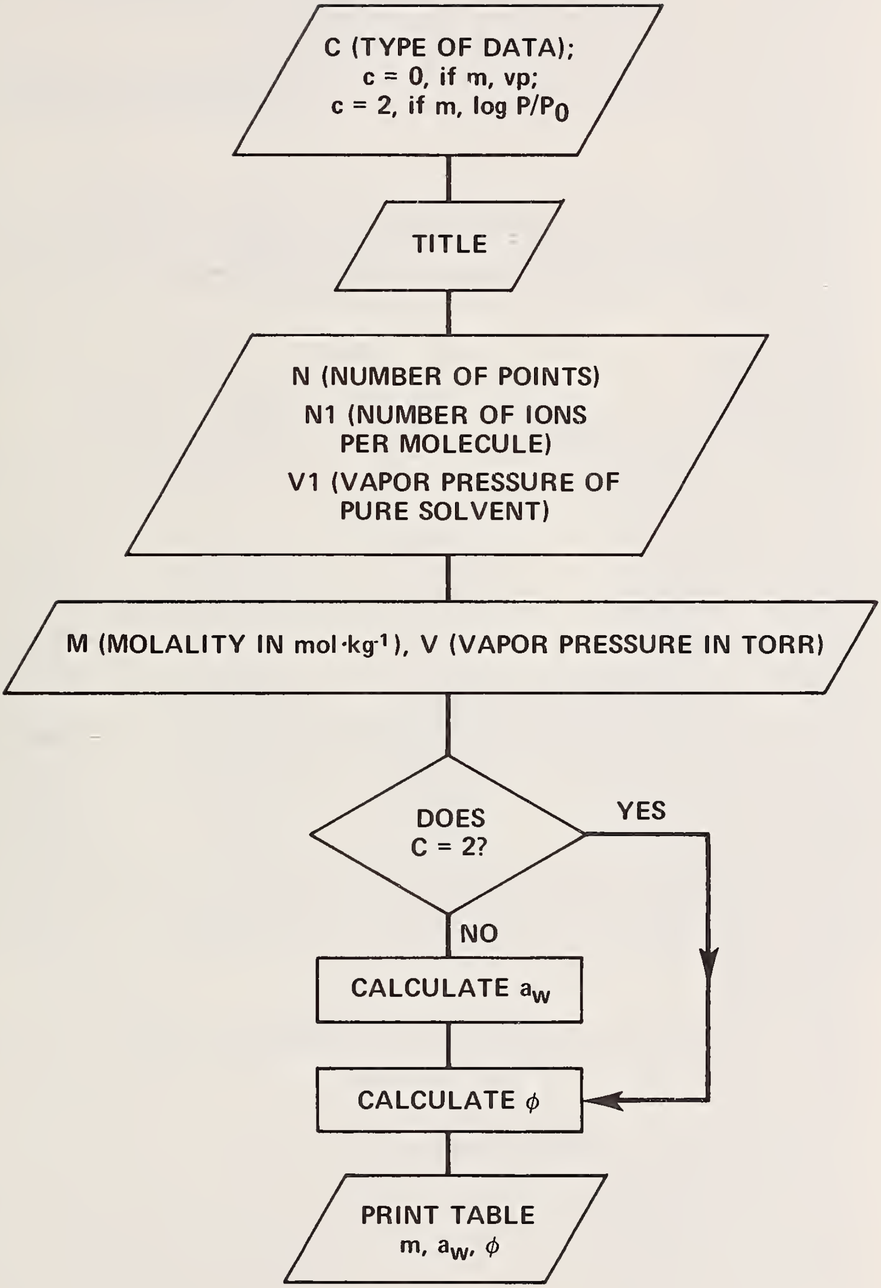

Fig. 1. Flow Diagram for: 'VAPOR'.

```
LIST 1

 76/09/15. 14.42.44.
PROGRAM   VAPOR

00100 REM:  B.STAPLES  X3632.   PROGRAM BSVAPOR
00110 REM:      VERSION 6-23-75.  (ADDS VP CORR. FOR NON-IDEAL H20)
00120 REM:   CALCULATES ACTIVITIES AND OSMOTIC COEFFICIENTS FROM
00130 REM:         VAPOR PRESSURE MEASUREMENTS.
00140 DIM M(100),F(100),V(100),P(100),L(100),A(100)
00150 DIM P1(100),A1(100)
00160 REM:  DATA BEGINS AT 1000//  TYPE OF DATA,TITLE,# POINTS, NU,
00170 REM:      VP REF.(V1), THEN SETS OF M, PRESSURE EVERY 10 LINES.
00180 READ C
00190 PRINT
00200 PRINT
00210 READ A$
00220 REM: A$ IS TITLE, C=2 IF DATA IN FORM OF MOLAL, LOG(P/P0).
00230 REM:  V=VAP. PRESS. ,  F=ACTIVITY H20,  P=PHI (OSMOTIC COEFF.)
00240 READ N,N1,V1
00250 PRINT " OSMOTIC COEFFICIENTS FROM VAPOR PRESSURE."
00260 PRINT " ========================================"
00270 PRINT
00280 PRINT
00290 PRINT A$
00300 PRINT
00310 PRINT "                               WITHOUT CORRECTION"
00320 PRINT"          WATER                 WATER"
00330 PRINT"MOLALITY  ACTIVITY      PHI     ACTIVITY      PHI"
00340 PRINT
00350 FOR I=1 TO N
00360 IF C=2 THEN 00390
00370 READ M(I),V(I)
00380 GO TO 00410
00390 READ M(I),L(I)
00400 GO TO 00440
00410 F(I)=V(I)/V1
00420 L(I)=LOG(F(I))
00430 GO TO 00460
00440 L(I)=L(I)*LOG(10)
00450 F(I)=10.↑(L(I)/LOG(10))
00460 P(I)=L(I)*(-55.508/(N1*M(I)))
00470 P1(I)=(55.508/(N1*M(I)))*(5.33464E-5*(V(I)-V1))
00480 A(I)=L(I)-5.33464E-5*(V(I)-V1)
00490 A1(I)=EXP(A(I))
00500 PRINT USING 00560,M(I);A1(I);P(I)+P1(I);F(I);P(I)
00510 NEXT I
00520 PRINT
00530 PRINT
00540 PRINT"REF. VP (H20, 25 DEG.) = "V1
00550 : #.#####        #.#####          #.#####        #.#####       #.#
00560:#.#####    #.#####    #.####     #.#####   ##.####
00570 : #.#####        #.#####
00580 PRINT
00590 PRINT
00600 PRINT
00610 FOR I=1 TO N
00620 PRINT FILE(TAPE 1) USING 00570,M(I);P(I)+P1(I)
00630 NEXT I
00640 PRINT
00650 PRINT
01000 DATA 0
01010 DATA CACL2      PETIT (1965)  VP
1020 DATA 13,3,23.7627
01030 DATA .25,23.480
01040 DATA .5,23.204
01050 DATA .75,22.791
01060 DATA 1,22.377
01070 DATA 1.5,21.460
01080 DATA 2,20.447
01090 DATA 2.5,19.183
01100 DATA 3,17.815
01110 DATA 3.5,16.277
01120 DATA 4,14.814
01130 DATA 4.5,13.295
01140 DATA 5,11.836
01150 DATA 6,9.272
9999 END
```

List 2

```
RUN

 76/05/04. 16.22.52.
PROGRAM   VAPOR


 OSMOTIC COEFFICIENTS FROM VAPOR PRESSURE.
 =========================================


CACL2      PETIT (1965)  VP

                                 WITHOUT CORRECTION
           WATER                  WATER
MOLALITY  ACTIVITY     PHI       ACTIVITY      PHI

  .25000    .98812     .8847      .98810      .8858
  .50000    .97652     .8793      .97649      .8804
  .75000    .95916    1.0287      .95911     1.0300
 1.00000    .94176    1.1103      .94169     1.1117
 1.50000    .90321    1.2558      .90310     1.2573
 2.00000    .86062    1.3887      .86047     1.3903
 2.50000    .80747    1.5827      .80727     1.5845
 3.00000    .74994    1.7748      .74970     1.7767
 3.50000    .68525    1.9981      .68498     2.0002
 4.00000    .62371    2.1836      .62341     2.1858
 4.50000    .55980    2.3855      .55949     2.3878
 5.00000    .49841    2.5768      .49809     2.5792
 6.00000    .39049    2.8998      .39019     2.9022

REF. VP (H20, 25 DEG.) =  23.7627




SS        0.469 SECS.

RUN COMPLETE.
```

5.2 Isopiestic Equilibration

In the isopiestic vapor equilibration method, a reference solution and another solution are allowed to come to equilibrium through the vapor phase, thus the activity of the solvent in the reference solution is equal to the activity of the solvent in the solution being determined. Analysis of each solution, after such equilibration, allows the determination of a set of isopiestic molalities.

Since the activity of the solvent, a_1, is equal in each solution, one can determine the osmotic coefficient, ϕ, from eq (13) by

$$\phi = \frac{\nu_r m_r \phi_r}{\nu m} , \qquad (14)$$

where the subscript r denotes values for the reference salt used.

The program "ISOPSTC" was designed to perform the calculation of ϕ from the isopiestic molalities determined experimentally.

5.2a. Program: ISOPSTC

General Description.

The program ISOPSTC, using the isopiestic molalities and the constants of eq (10) for calculating ϕ_r, calculates ϕ by means of eq (14). The procedure is diagrammatically presented in figure 2. It should be noted that "ISOPSTC" can be also incorporated in the more complex evaluation program "EVALU", discussed later. A separate and self-contained listing is presented as list 3. List 4 illustrates a sample program run for "ISOPSTC". Table 1 gives the codes used to designate each charge-type.

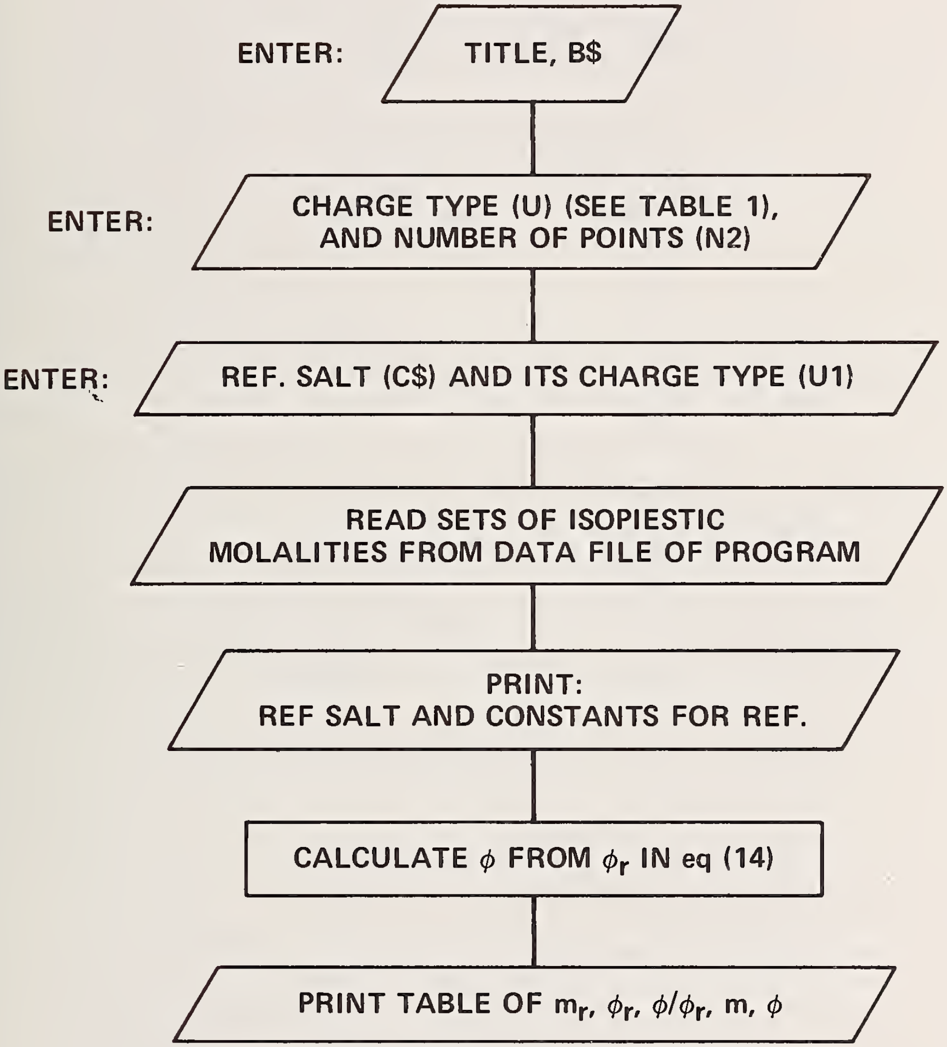
ENTER:
TITLE, B$
ENTER:
CHARGE TYPE (U) (SEE TABLE 1), AND NUMBER OF POINTS (N2)
ENTER:
REF. SALT (C$) AND ITS CHARGE TYPE (U1)
READ SETS OF ISOPIESTIC MOLALITIES FROM DATA FILE OF PROGRAM
PRINT: REF SALT AND CONSTANTS FOR REF.
CALCULATE ϕ FROM ϕ_r IN eq (14)
PRINT TABLE OF m_r, ϕ_r, ϕ/ϕ_r, m, ϕ

Fig. 2. Flow Diagram for : 'ISOPSTC'.

Table 1. Designation of Charge-Type Code

Charge-type Selection code	Ionic Strength factor $I/m = [\frac{1}{2}\sum_i \nu_i z_i^2]$	$\lvert z_+ z_- \rvert$	ν	Salt type
1	1	1	2	1-1
2	3	2	3	1-2; 2-1
3	6	3	4	1-3; 3-1
4	10	4	5	1-4; 4-1
5	4	4	2	2-2
6	15	6	5	2-3; 3-2
7	12	8	3	2-4; 4-2
8	9	9	2	3-3
9	42	12	7	3-4; 4-3
10	16	16	2	4-4

LIST 3.

```
 76/09/15. 14.47.23.
PROGRAM    ISOPSTC

00100 REM*** PROGRAM TO CALCULATE OSMOTIC COEFFICIENTS FROM
00110 REM;          ISOPIESTIC MOLALITIES.
00120 REM:    VERSION 10-3-75.
00130 REM:    ENTER CONSTANTS FOR REFERENCE SALT FOR HAMER-WU EQN.
00135 REM:        AT LINE NO. 1000.
00140 REM: TAPE1 IS THE DATA FILE OF ISOPIESTIC MOLALITIES
00150 REM: M REF. ,  M 'UNKNOWN'
00160 REM:  U IS CHARGE TYPE,  N1 IS THE NO. OF DATA POINTS.
00170 REM:  CHARGE TYPE SPECIFIED ACCORDING TO TABLW 1 IN TEXT:
00180 REM: 1 (1:1 SALT); 2 (2:1, 1:2); 3 (3:1, 1:3); 4 (4:1, 1:4)
00185 REM: ETC.
00190 DIM M1(300),M2(300),P1(300),P2(300),P3(300),G1(300),G2(300),G3(300)
00200 DIM D2(300),D4(300),D5(300),Y(300),X(300),W(300)
00210 DIM P9(300)
00220 REM: R(I)= IONIC STRENGTH;  Q(I)= CHARGE  OF CATION;  AND
00230 REM:   T(I)= NU, THE TOTAL NO. OF IONS SALT PRODUCES.
00240 FOR I=1TO 10
00250 READ R(I),Q(I),T(I)
00260 NEXT I
00270 A=.51084
00280 A4=A*(LOG(10))
00290 PRINT
00300 PRINT" TITLE:"INPUT B$
00310 PRINT
00320  PRINT"ENTER CHARGE TYPE (SEE TABLE 1 IN TEXT) , NO. POINTS:"
00330 INPUT U,N1
00340 PRINT
00350 PRINT
00360 PRINT" REF. SALT, AND ITS CHARGE TYPE "INPUT C$, U1
00370 FOR I=1TO8
00380 READ A1(I)
00390 NEXT I
00400 PRINT
00410 PRINT
00420 REM: A1(I) ARE THE CONSTANTS FOR THE REFERENCE SALT IN EQN.
00430 REM: M1, M2 ARE ISOPIESTIC MOLALITIES (M1=REF.)
00440 FOR I=1TO N1
00450 INPUT FILE(TAPE1) M1(I),M2(I)
00460 NEXT I
00470A3=A4*Q(U1)*SQR(R(U1))
00480 A1(1)=A1(1)*SQR(R(U1))
00490 PRINT
00500 PRINT" REFERENCE IS  "; C$
00510 PRINT
00520 PRINT"CONSTANTS USED FOR REFERENCE:"
00530 PRINT
00540 FOR I=1TO8
00550 PRINT A1(I),
00560 NEXT I
00570 PRINT
00580 PRINT
00585 PRINT B$
00590 PRINT
00595 PRINT
00600 PRINT "M1 (REF)","PHI1 (REF)";"  PHI/PHI(REF)","  M2","PHI"
00610 PRINT
00620 FOR I=1TO N1
00630 D1=SOR(M1(I))
00640D3=1+A1(1)*D1
00650 P1(I)=1-A3*(D3-2*LOG(D3)-1/D3)/A1(1)↑3/M1(I)
00660FORJ=2TO8
00670 P1(I)=P1(I)+(LOG(10))*A1(J)*M1(I)↑(J-1)*(J-1)/J
00680NEXTJ
00690 P2(I)=P1(I)*M1(I)*T(U1)/M2(I)/T(U)
00700 P9(I)=P2(I)/P1(I)
00710 PRINT USING 00730,M1(I),P1(I),P9(I),M2(I),P2(I)
00715 PRINT FILE(TAPE2) M2(I);P2(I)
00720 NEXTI
00730 :##.####        ##.####          #.#####          ##.####          ##.####
00740 REM:  OUTPUT FORMATS ARE SPECIFIED BY LINE BEGINNING WITH  " : ".
00750 PRINT
00760 PRINT
00770 REM: FIRST SET OF DATA ARE PROPER FACTORS FOR IONIC STRENGTH CALCN,
00780DATA1,1,2,3,2,3,6,3,4,10,4,5,4,4,2,15,6,5,12,8,3,9,9,2,42,12,7,16,16,2
1000 DATA 1.295, 7.E-5, 3.5990E-3, -1.94540E-4, 0,0,0,0
9999 END
READY.
```

List 4

```
GET,TAPE1=ROBSULP
READY.

RUN

 76/05/04. 16.41.10.
PROGRAM   ISOPSTC


 TITLE: ? H2SO4    ROBINSON

ENTER CHARGE TYPE (SEE TABLE 1 IN TEXT) , NO. POINTS:
?  2,10


 REF. SALT, AND ITS CHARGE TYPE ? KCL, 1



 REFERENCE IS  KCL

CONSTANTS USED FOR REFERENCE:

 1.295            .00007           .003599          -1.94540E-4      0
 0                0                0

H2SO4    ROBINSON


M1 (REF)         PHI1 (REF)  PHI/PHI(REF)         M2              PHI

  .2140           .9120        .73313            .1946            .6686
  .2434           .9098        .73324            .2213            .6671
  .3885           .9028        .74106            .3495            .6691
  .4036           .9024        .74451            .3614            .6718
  .5446           .8993        .75138            .4832            .6757
  .6647           .8981        .75970            .5833            .6823
  .7268           .8977        .75993            .6376            .6822
  .8200           .8976        .76984            .7101            .6910
  .8702           .8976        .77434            .7492            .6951
  .9245           .8978        .77938            .7908            .6997


SS      0.496 SECS.

RUN COMPLETE.
```

6. Experimental Methods for Measuring the Activity of the Solute

6.1 Electromotive Force of Galvanic Cells without Liquid-Junction

There are two types of cells without liquid junction:

A. Single fluid cells and B. Two-fluid cells.

6.1a. Single-fluid cells

For the cells of the type

$$\mathrm{M(Hg)_x(\ell)\,|\,MX(m);\ AgX(s),\ Ag(s),} \tag{15}$$

using the expression in eq (6) to represent $a_\pm$, the emf can be expressed by

$$E = E° - \frac{\nu RT}{nF} \ln m_\pm \gamma_\pm \tag{16}$$

Hereafter γ will be used to represent $\gamma_\pm$.

Substituting for $m_\pm$ from eq (6) one then obtains

$$E = E° - \frac{\nu RT}{nF} \ln\left[\left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)^{1/\nu} m\gamma\right] \tag{17}$$

from which γ may be calculated.

Using one molality as a reference, eq (16) can be rewritten as

$$E - E_r = \frac{\nu RT}{nF} \ln \frac{m\gamma}{(m\gamma)_r} \tag{18}$$

where E_r is the emf of the cell at reference molality, m_r, and γ_r is the reference activity coefficient at that molality.

6.1b. Two-fluid cells

A representative example of a two-fluid galvanic cell is

$$\mathrm{Ag(s),\ AgCl(s);\ MCl\ \ (m)\,|\,M_xHg(\underset{\sim}{\ell})\,|\,MCl\ \ (m_r);\ AgCl(s),\ Ag(s).} \tag{19}$$

The emf of this cell is

$$E = + \frac{\nu RT}{nF} \ln \left[\frac{m\gamma}{(m\gamma)_r}\right] \tag{20}$$

6.1c. Program: EMF

General Description

This program calculates mean activity coefficients, $\gamma_\pm$, from emf measurements without liquid-junction based on a reference molality and a reference activity coefficient. Differences between the emf, E, at each molality, and the emf, E_r, at the reference molality are computed and $\gamma_\pm$ is derived from eqs (18, 20) in this manner. Data from one-fluid or two-fluid cells can be used in this program. Corrections are applied to the voltage measurements, if needed, to convert the emf from international volts to volts. The procedure used is presented as a flow diagram in fig 3, and the program "EMF" is shown in list 5. List 6 is a sample run for a single fluid cell and list 7 is a sample for a two-fluid cell.

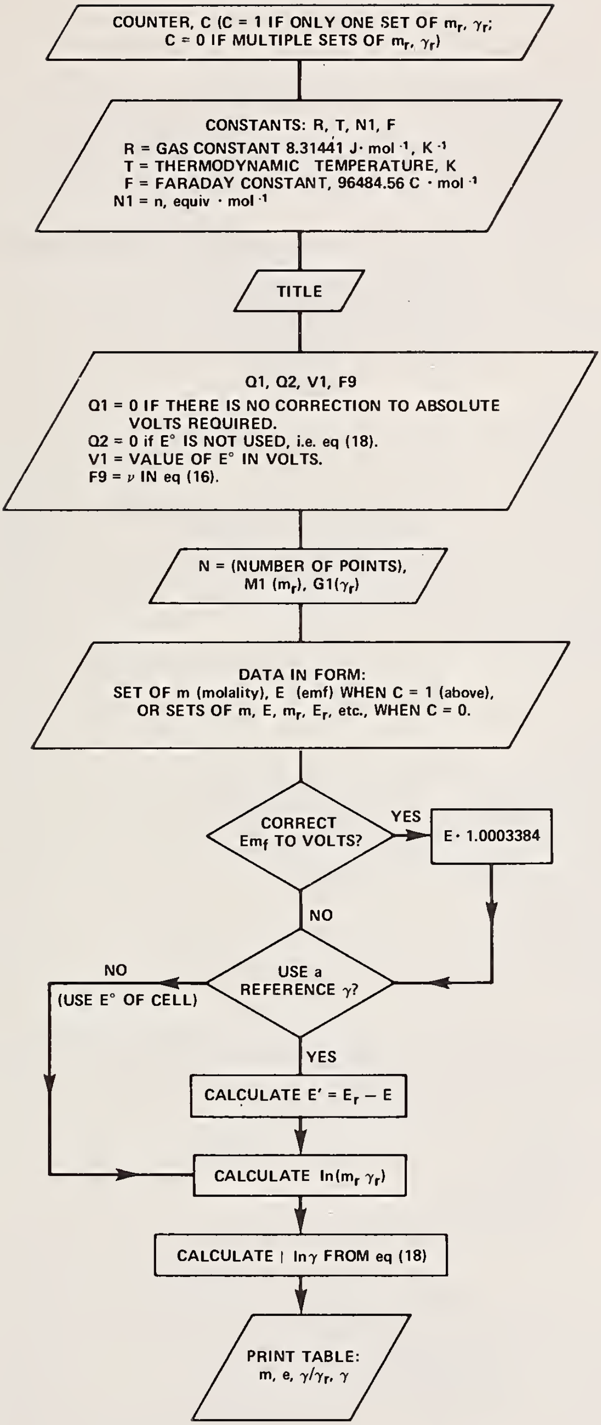
COUNTER, C (C = 1 IF ONLY ONE SET OF m_r, γ_r; C = 0 IF MULTIPLE SETS OF m_r, γ_r)
CONSTANTS: R, T, N1, F
R = GAS CONSTANT 8.31441 $J \cdot mol^{-1}$, K^{-1}
T = THERMODYNAMIC TEMPERATURE, K
F = FARADAY CONSTANT, 96484.56 $C \cdot mol^{-1}$
N1 = n, equiv $\cdot$ mol^{-1}
TITLE
Q1, Q2, V1, F9
Q1 = 0 IF THERE IS NO CORRECTION TO ABSOLUTE VOLTS REQUIRED.
Q2 = 0 if E° IS NOT USED, i.e. eq (18).
V1 = VALUE OF E° IN VOLTS.
F9 = ν IN eq (16).
N = (NUMBER OF POINTS), M1 (m_r), G1(γ_r)
DATA IN FORM:
SET OF m (molality), E (emf) WHEN C = 1 (above),
OR SETS OF m, E, m_r, E_r, etc., WHEN C = 0.
CORRECT E_{mf} TO VOLTS?
YES
$E \cdot 1.0003384$
NO
USE a REFERENCE γ?
NO
(USE E° OF CELL)
YES
CALCULATE $E' = E_r - E$
CALCULATE $\ln(m_r \gamma_r)$
CALCULATE | $\ln\gamma$ FROM eq (18)
PRINT TABLE:
m, e, γ/γ_r, γ

Fig. 3. Flow Diagram for : 'EMF'.

```
LIST 5,

 76/09/15. 14.35.54.
PRDGRAM       EMF

00100 REM***B. STAPLES  X3632
00110 REM:  VERSIDN 3-20-75.
00120 REM: DATA BEGINS AT 1000// IDENTIFIER,CONSTANTS,IDENTIFIERS,
00130 REM:     M, EMF (DR M(REF), GAM(REF);  M, EMF) 1 PAIR PER LINE
00140 REM:     EVERY 10 LINE #S ...
00150 REM***510 M, EMF   ETC.  1 SET PER LINE, EVERY 10 LINES $***
00160 DIM M(50),E(50),G(50),L(50),A(50)
00170 DIM M1(50),G1(50)
00180 PRINT"======================================================"
00190 PRINT"   CALCULATIDN DF ACTIVITY CDEFFICIENTS FRDM EMF DATA."
00200 PRINT
00210 REM: IF DNE REF. M AND GAMMA ;  SET C=1
00220 REM: IF MDRE THAN A SINGLE REF. M AND GAM.;  SET C=0
00230 READ C
00240 READ R,T,N1,F
00250 READ A$
00260 PRINT A$
00270 PRINT
00280 IF C=1 THEN 00330
00290 PRINT" REFERENCE   REFERENCE"
00300 PRINT"  MOLALITY      GAMMA        MDLALITY      EMF (MEAS.)  GAM/GAM",
00310 PRINT"(R)    GAMMA"
00320 GD TD 00350
00330 PRINT" MOLALITY              GAMMA        LDG(GAMMA)     EMF (MEAS.)";
00340 PRINT"    GAM/GAM(REF.)"
00350 PRINT
00360 REM: Q1=0 (ND CDRR. TO ABS. VDLTS); Q2=0 (NO E ZERO); V1=E ZERD
00370 READ Q1,Q2,V1,F9
00380 READ N,M1,G1
00390 K=R*T*(LOG(10))/(N1*F)
00400 REM: PROPER FACTOR (F9) NEEDED ACCORDING TO CELL EQUATION; N1=NU
00410 K=F9*K
00420 FOR I=1 TD N
00430 IF C=1 THEN 00450
00440 READ M1,G1
00450 READ M(I),E(I)
00460 IF Q1=0 THEN 00480
00470 E(I)=E(I)*1.0003384
00480 IF Q2=0 THEN 00500
00490 E(I)=V1-E(I)
00500 S=LDG(M1*G1)/LDG(10)
00510 L(I)=(E(I)/K) +S -LOG(M(I))/LDG(10)
00520 G(I)=10↑L(I)
00530 IF C=1 THEN 00560
00540 PRINT USING 00600, M1,G1,M(I),E(I),G(I)/G1,G(I)
00550 GD TO 00570
00560 PRINT USING 00590, M(I),G(I),L(I),E(I),G(I)/G1
00570 PRINT FILE(TAPE1) M(I),G(I)
00580 NEXT I
00590 : ##.######        ##.####        -#.######     -#.######      #.#####
00600 : ##.######    #.####        #.######        -#.######     #.#####       #.###
00610 REM: IF DUTPUT TAPE OF M, GAM. REQUIRED, AT END DF RUN TYPE:
00620 REM:        SAVE,TAPE1=(FILE NAME)
00630 PRINT
00640 PRINT
00650 IF C=0 THEN 00670
00660 PRINT"REF. MDLALITY = "M1"      REF. GAMMA = "G1
00670 PRINT
00680 IF Q1=0 THEN 00700
00690 PRINT "  EMF CORRECTED TD ABS. VOLTS."
00700 PRINT"     ======================================"
00710 PRINT
00720 PRINT
00730 REM: VALUES DF FUNDAMENTAL CDNSTANTS FRDM CDHEN + TAYLDR,
00740 REM: J. PHYS.CHEM. REFERENCE DATA, 2, 663 (1972).
01000 DATA 1
01010 DATA 8.31441,298.15,2,96484.56
01020 DATA  CACL2   SCATCHARD+TEFFT (1930)
01030 DATA 1,0,0,3
01040 DATA 9,.10029,.5214
01050 DATA  .009921,  -.0761
01060 DATA .010509,-.0742
01070 DATA .02594,-.0439
01080 DATA .02758,-.0412
01090 DATA .04113,-.02982
01100 DATA .12634,.0078
01110 DATA .4420,.0558
01120 DATA .6589,.0768
01130 DATA .9301,.09615
99999 END
```

List 6

```
RUN

 76/05/05. 09.34.15.
PROGRAM   BRSEMF

======================================================
   CALCULATION OF ACTIVITY COEFFICIENTS FROM EMF DATA.

CACL2   SCATCHARD+TEFFT (1930)

 MOLALITY          GAMMA       LOG(GAMMA)    EMF (MEAS.)   GAM/GAM(REF.)

   .009921         .7312        -.135986     -.076126     1.40231
   .010509         .7251        -.139574     -.074225     1.39077
   .025940         .6450        -.190417     -.043915     1.23712
   .027580         .6507        -.186605     -.041214     1.24803
   .041130         .5863        -.231885     -.029830     1.12446
   .126340         .5068        -.295184      .007803      .97195
   .442000         .5035        -.297972      .055819      .96573
   .658900         .5826        -.234640      .076826     1.11735
   .930100         .6820        -.166222      .096183     1.30800

REF. MOLALITY =  .10029      REF. GAMMA =  .5214

  EMF CORRECTED TO ABS. VOLTS.
    ======================================



SS       0.371 SECS.

RUN COMPLETE.
```

List 7

```
OLD
FILE NAME:     EMF

TAPE

01020 DATA  CACL2     FOSBINDER (1929)
01030 DATA 1,0,0,3
01040 DATA 11,.0099,.73035
01050 DATA .0435,.04870
01060 DATA .0628,.06070
01070 DATA .0781,.06885
01080 DATA .0897,.06685
01090 DATA .1411,.08940
01100 DATA .3069,.11735
01110 DATA .7158,.15605
01120 DATA 1.2081,.18289
01130 DATA 1.5378,.20232
01140 DATA 1.9833,.21702
01150 DATA 3.502, .30047
NOR
READY.
```

```
RUN

 76/05/05. 13.51.57.
PROGRAM      EMF

==================================================
   CALCULATION OF ACTIVITY COEFFICIENTS FROM EMF DATA.

CACL2    FOSBINDER (1929)

 MOLALITY            GAMMA        LOG(GAMMA)     EMF (MEAS.)    GAM/GAM(REF.)

   .043500            .5884         -.230338       .048716        .80562
   .062800            .5565         -.254535       .060721        .76196
   .078100            .5529         -.257353       .068873        .75704
   .089700            .4570         -.340040       .066873        .62579
   .141100            .5217         -.282573       .089430        .71433
   .306900            .4955         -.304968       .117390        .67842
   .715800            .5801         -.236506       .156103        .79426
  1.208100            .6898         -.161255       .182952        .94453
  1.537800            .8974         -.047022       .202388       1.22870
  1.983300           1.0191          .008200       .217093       1.39530
  3.502000           5.0348          .701986       .300572       6.89375

REF. MOLALITY =  .0099       REF. GAMMA =  .73035

  EMF CORRECTED TO ABS. VOLTS.
    ===================================



SS       0.446 SECS.

RUN COMPLETE.
```

6.2 Electromotive Force of Galvanic Cells With Transference

A cell with transference can be illustrated as

$$\text{Ag(s), AgCl(s); MCl}(m_r)|\text{MCl(m); AgCl(s), Ag(s)}$$

The emf of this cell is given by

$$E = -\frac{\nu RT}{nF}\int_{m_r}^{m} t_+ \; d[\ln\,(m\gamma)] \tag{21}$$

where t_+ is the cation transference number.

The integration required is carried out in the program 'TRFNO' by means of the following procedure. Since t_+ usually varies only slightly as a function of molality, following Robinson and Stokes [5] we define x by the equation

$$\frac{1}{t_+} = \frac{1}{t'_+} + x \tag{22}$$

Here t'_+, is the transference number at a reference molality, m', x will be only a small fraction of $1/t'_+$. Hence:

$$-d\,\log\,(m\gamma) = \frac{1}{2k}\left(\frac{1}{t'_+}\,dE + x dE\right) \tag{23}$$

where

$$k = \nu RT(\ell n10)/nF \tag{24}$$

This can be integrated between m and m' to give, since E = 0 when m = m':

$$-\log\left(\frac{\gamma m}{\gamma' m'}\right) = \frac{E}{kt'_+} + \frac{1}{k}\int_{m'}^{m} x dE \tag{24}$$

In this manner, the integral in eq (24) is quite small and can easily be evaluated by graphical or numerical integration without introducing inaccuracies in the activity coefficient.

6.2a. Program: TRFNO

General Description

The program 'TRFNO', calculates the activity coefficient ratio γ/γ_r, where γ_r is the activity coefficient at the reference molality, from the transference number and emf of cells with liquid-junction. The procedure is diagrammatically shown in figure. 4. The program listing (list 8) follows the flow diagram and a sample output is shown as list 9.

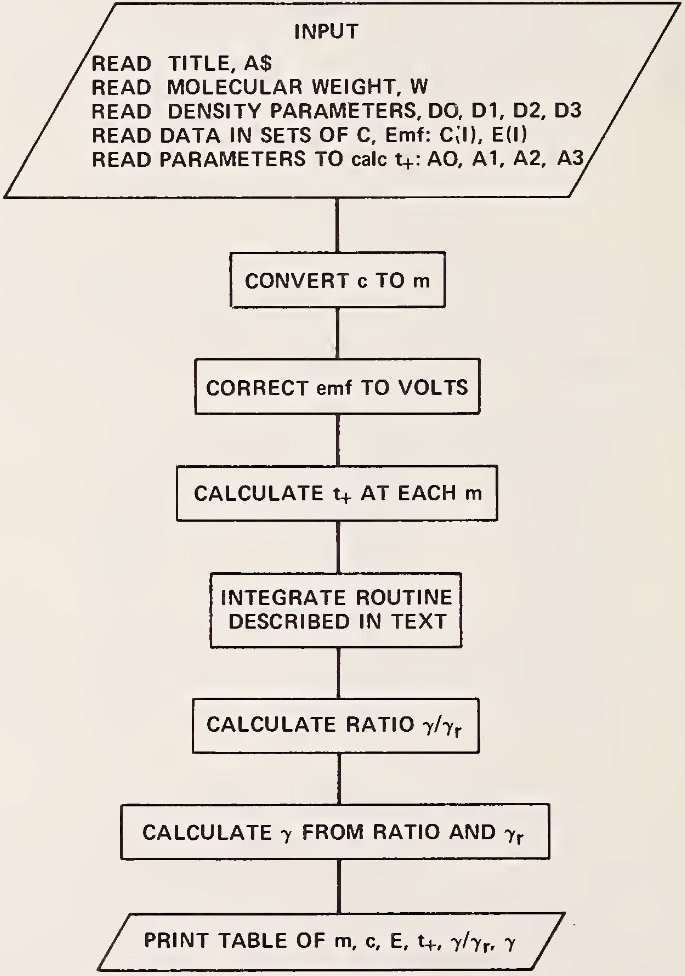
INPUT
READ TITLE, A$
READ MOLECULAR WEIGHT, W
READ DENSITY PARAMETERS, DO, D1, D2, D3
READ DATA IN SETS OF C, Emf: C(I), E(I)
READ PARAMETERS TO calc t+: AO, A1, A2, A3
CONVERT c TO m
CORRECT emf TO VOLTS
CALCULATE t+ AT EACH m
INTEGRATE ROUTINE DESCRIBED IN TEXT
CALCULATE RATIO γ/γr
CALCULATE γ FROM RATIO AND γr
PRINT TABLE OF m, c, E, t+, γ/γr, γ

Fig. 4. Flow Diagram for : 'TRFNO'.

List 8

```
LIST

 76/05/05. 13.25.03.
PROGRAM    TRFNO

10 REM PROGRAM NCCWT3 CALCULATES ACTIVITY COEFFICIENT RATIOS,
11 REM GAMMA/GAMMA(REF), FROM DATA FROM MEASUREMENTS OF EMF OF
12 REM CONCENTRATION CELLS WITH TRANSFERENCE. FOR EXAMPLE:
13 REM AG-AGCL/CACL2(M(REF))//CACL2(M)/AGCL-AG        (1)
14 REM AUXILIARY DATA NEEDED ARE TRANSFERENCE NUMBERS AND DENSITIES.
15 REM TRANSFERENCE NUMBERS ARE CALCULATED FROM AN EQUATION:
16 REM T(+)=K0+K1*C↑.5+K2*C+K3*C↑1.5                      (2)
17 REM IN WHICH C IS EQUIVELANTS PER LITER.
18 REM DENSITY IS CALCULATED FROM AN EQUATION:
19 REM D=D0+D1*C+D2*C↑1.5                                 (3)
20 REM IN WHICH C IS MOLARITY, (MOLES/LITER).
21 REM DATA ARE GIVEN IN LINE 5000 AND FOLLOWING IN ORDER:
22 REM A$=TITLE
23 REM N5=NU IONS/MOLECULE.
24 REM N6=N EQUIVELANTA/MOLE
25 REM W=MOLECULAR MASS.
26 REM D0,D1,D2 ARE COEFFICIENTS IN DENSITY EQUATION (3).
27 REM N9=NUMBER OF SETS OF DATA.
28 REM FOR EACH SET OF DATA:
29 REM      A$(J)=TITLE OF DATA SET, J.
30 REM      B$(J)=CONCENTRATION UNITS OF DATA SET J. C=MOLARITY,M=MOLALIY
31 REM      K(J)=UNITS OF EMF DATA. 1=VOLTS,0=VOLTS(INTERNATIONAL).
32 REM      N(J)=NUMBER OF POINTS IN DATA SET J.
33 REM      M1(J)=REFERENCE CONCENTRATION FOR DATA SET J.
34 REM      M(I),E(I)=N(J) PAIRS OF CONCENTRATION-EMF DATA.
35 REM K0,K1,K2,K3 ARE COEFFICIENTS FOR TRANSFERENCE NUMBER EQ. (2).
100 DIM M(50),C(50),D(50),M1(50)
102 DIME(50)
110 DIM K(50),L(50),A(50)
112 DIM X1(50),X2(50),X3(50),X(50),Y(50)
114 DIM G1(50),G2(50),G3(50),G4(50),G5(50),G6(50)
120 READ A$
122 READ N5,N6
124 LET B=.0256918359
125 LET B=B*N5/N6
126 LET B=1/B
130 READW
140 READ D0,D1,D2
150 LET N(0)=0
155 READN9
160 FOR J=1 TO N9
165 READ A$(J)
166 READ B$(J)
167 READ K(J)
170 READ N(J)
175 LET N(J)=N(J-1)+N(J)
180 READ M1(J)
185 FOR I=N(J-1)+1 TO N(J)
190 READ M(I),E(I)
192 IF K(J)=0 THEN 195
193 LET E(I)=E(I)*1.0003384
195 NEXT I
200 NEXT J
210 LET N=N(N9)
240 READ K0,K1,K2,K3
245 GOTO 275
```

List 8 cont.

```
250 FOR J=1 TO N9
252 LET M1(J)=M1(J)*1E-4
254 NEXT J
270 FOR I= 1 TO N
271 LET M(I)=M(I)*1E-4
272 LET E(I)=E(I)*1E-3
273 LET E(I)=-E(I)
274 NEXT I
275 FOR J=1 TO N9
278 IF B$(J)="C" THEN 400
279 FOR I=N(J-1)+1 TO N(J)
280 LET M=M(I)
290 GOSUB 1500
300 LET D(I)=D
310 LET C(I)=C
320 NEXT I
340 LET M=M1(J)
350 GOSUB 1500
360 LET D1(J)=D
370 LET C1(J)=C
380 GOTO 510
400 FOR I=N(J-1)+1 TO N(J)
405 LET C(I)=M(I)
410 LET C=C(I)
420 GOSUB 2000
430 LET M(I)=M
440 LET D(I)=D
450 NEXT I
460 LET C1(J)=M1(J)
470 LET C=M1(J)
480 GOSUB 2000
490 LET M1(J)=M
500 LET D1(J)=D
510 NEXT J
515 GOTO 680
550 FOR J=1 TO N9
560 FOR I=N(J-1)+2 TO N(J)
570 LET E(I)=E(I)+E(I-1)
580 NEXT I
590 NEXT J
680 FOR I=1 TO N
700 LET C=N6*C(I)
710 GOSUB 2200
720 LET K(I)=K
750 NEXT I
755 FOR J=1 TO N9
760 LET C=N6*C1(J)
770 GOSUB 2200
780 LET R1(J)=K
810 NEXT J
855 FOR J=1 TO N9
860 FOR I=N(J-1)+1 TO N(J)
862 IF M(I)<M1(J) THEN 880
864 LET J(J)=I
870 GOTO 890
880 NEXT I
890 NEXT J
960 FOR J=1 TO N9
965 FOR I=N(J-1)+1 TO N(J)
970 LET X(I)=1/K(I)-1/R1(J)
975 NEXT I
980 NEXT J
```

List 8 cont.

```
985 FOR J=1  TO N9
990 GOSUB 2500
1040 FOR I=N(J-1)+1  TO N(J)
1050 LET G1(I)=LOG(M1(J)/M(I))-B*E(I)/R1(J)-B*Y(I)
1060 LET G2(I)=EXP(G1(I))
1070 NEXT I
1080 NEXT J
1230 PRINT"CONCENTRATION CELLS WITH TRANSFERENCE ";A$
1240 PRINT
1250 PRINTUSING 4010
1255 PRINT
1260 FOR J=1  TO N9
1265 PRINTUSING4000,M1(J),C1(J)," ",R1(J)
1270 NEXT J
1272 PRINT
1275 PRINT
1278 FOR J=1  TO N9
1280 FOR I=N(J-1)+1  TO N(J)
1282 PRINTUSING 4000,M(I),C(I),E(I),K(I),G1(I),G2(I)
1284 NEXT I
1286 PRINT
1288 NEXT J
1290 FOR I= 1 TO N
1300 PRINT:NDTG: M(I);G2(I)
1310 NEXT I
1320 RESTORE:NDTG:
1490 GO TO 9999
1499 REM:SUBROUTINE 1500 TO 1560 CALCULATES C AND D FROM M.
1500 LET D=D0
1510 LET D3=D
1520 LET C=M*D3/(1+W*M/1000)
1530 LET D=D0+D1*C+D2*C↑1.5
1540 IF ABS(D-D3)<1E-6 THEN1560
1550 GO TO 1510
1560 RETURN
1999 REM: SUBROUTINE2000 TO 2020 CALCULATES M SND D FORM C
2000 LET D=D0+D1*C+D2*C↑1.5
2010 LET M=C/(D-W*C/1000)
2020 RETURN
2199 REM: SUBROUTINE 2200 TO 2230 CALCULATES TRANSFERENCE NUMBERS.
2200 LET K=K0+K1*SQR(C)+K2*C+K3*C↑1.5
2230 RETURN
2499 REM:SUBROUTINE 2500 TO 2580 CALCULATES INTEGRAL OF X DE
2500 LET N3=N(J)
2510 LET N4=N(J-1)+1
2520 LET P=J(J)
2530 GOSUB 3000
2580 RETURN
3000 LET Y(P)=X(P)*E(P)/2
3010 FOR Q=P+1  TO N3
3020 LET Y(Q)=Y(Q-1)+(X(Q)+X(Q-1))*(E(Q)-E(Q-1))/2
3030 NEXT Q
3040 LET Y(P-1)=X(P-1)*E(P-1)/2
3050 FOR Q=P-2  TO N4 STEP-1
3060 LET Y(Q)=Y(Q+1)+(X(Q)+X(Q+1))*(E(Q)-E(Q+1))/2
3070 NEXT Q
3080 RETURN
4000:##.######   ##.######   -##.######   #.######   -#.######   ##.######
4010:    M          C           E           T         LN(G/GR))   G/G(R)
```

List 8 cont.

```
5000 DATA CACL2   LUCASSE TRANSF. CELL  1925
5005 DATA 3,2
5010 DATA 110.986
5020 DATA .99707,.0924,-.0042
5025 DATA 1
5030 DATA G1,M,0,11
5040 DATA 0.01
5045 DATA .01547, .00601,  .02006, .00974
5047 DATA .03955, .01898,  .04966, .02198
5049 DATA .08053, .02841, .1612, .03683
5050 DATA .3208, .04600, .6162, .05487
5060 DATA 1.013, .06264
5065 DATA 1.600, .07164
5070 DATA 2.586, .08357
7120 DATA.4392,-.1375,.1620,-.1660
9999 END
```

List 9

```
RUN

 76/05/05. 13.35.38.
PROGRAM  TRFNO

CONCENTRATION CELLS WITH TRANSFERENCE CACL2   LUCASSE TRANSF. CELL  1925

   M           C             E            T        LN(G/GR))    G/G(R)

 .010000     .009969                   .422547


 .015470     .015420      .006010     .419150    -.806887     .446245
 .020060     .019994      .009740     .416855   -1.298263     .273006
 .039550     .039404      .018980     .409694   -2.557303     .077514
 .049660     .049467      .021980     .406813   -2.975619     .051016
 .080530     .080166      .028410     .399460   -3.872962     .020797
 .161200     .160204      .036830     .383168   -5.125562     .005943


SS        0.790 SECS.

RUN COMPLETE.
```

7. Fitting the Data

7.1a. Program: EVALU

The program EVALU is a non-linear least squares fit of the data, eqs (9,10). The program fits Y (either ϕ or ln γ or both) as a function of molality (eqs 9 or 10) for a set of experimental points.

Factors for different charge-type salts are read into the program (see table 1) then the letters designating the parameters (B, C, D, etc) for eqs (9, 10). The title is inputted via a conversational mode followed by the charge-type code (see table 1) the number of ϕ data points, N1; the number of γ points, N2, the number of parameters, L, and the number of iterations, S.

The specified number of m, ϕ data pairs, N1 are read from a file (TAPE3) or can be read from within the program data statements if this command is changed to a simple read statement. This read statement is skipped if N1 = 0.

Next the number of m, γ data pairs, N2, are read from a file (TAPE4). This statement can also be modified to a simple read statement. This read statement is skipped if N2 = 0. The program prints out the original data before starting the calculations; it is recommended that these print statements be deleted or by-passed to save time, particularly if large data files are being read.

The initial estimates for each of the 8 parameters are read, any except the first, B, may be zero. Then an alphanumeric statement 'TEST' is read to insure that the proper data format has been followed up to this point. Various terms of eq (11) are calculated, plus the deviations and the standard deviation. Then a fitting procedure is performed, the parameters are incremented, and the calculation of fit is repeated for the specified number of iterations. Finally, a table of m, Y (ϕ and/or ln ϕ) and, ΔY is printed, along with two calculated output files TAPE1: m, ϕ (calculated) and TAPE2: m, γ (calculated). These output files may then be saved on line and used in future calculations.

The flow diagram, figure 5, and listing, list 10, of the program follow. An example of the output of EVALU is shown in list 11.

A warning that users should note is that errors may probably result from putting this program on a computer with 32 or 36 bit words instead of a CDC computer with 60 bit words, due to the matrix inversion used.

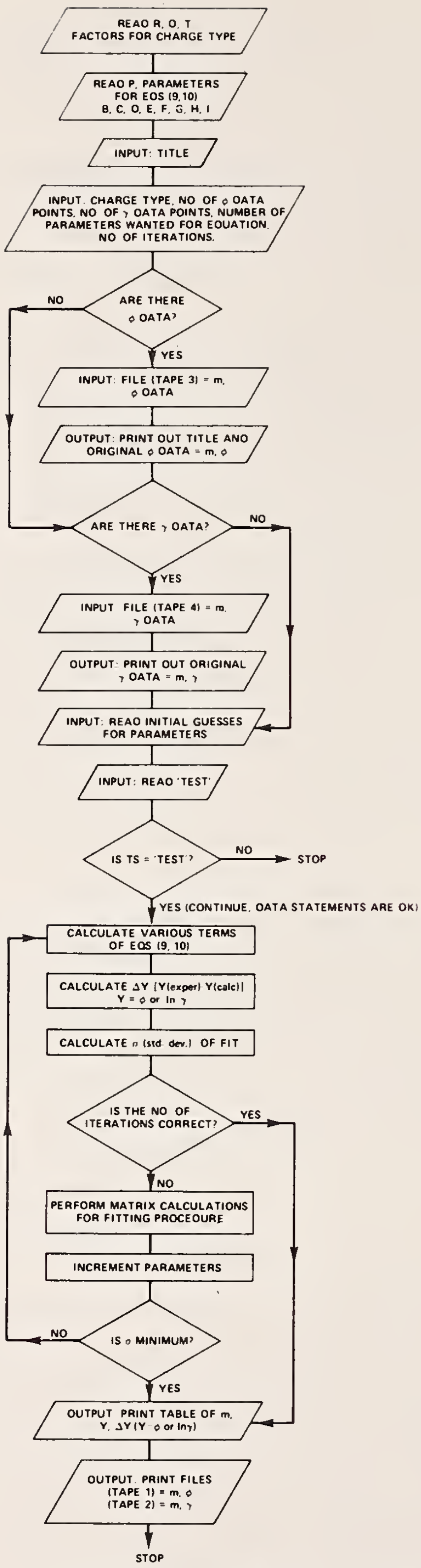

Fig. 5. Flow Diagram for : 'EVALU'.

List 10

```
LIST


 76/05/04. 10.28.09.
PROGRAM    EVALU

00100 REM*** B. STAPLES X3632.  PROGRAM TO FIT PHI AND GAMMA DATA.
00110 REM*** VERSION 1-28-75.  DATA FROM FILES, AND INPUT SOME.
00120 REM* TAPE3= PHI DATA FILE;  TAPE4= GAMMA DATA FILE.
00130 REM* U=CHARGE TYPE (Z+),N1=# PHI 'S, N2=# GAMMA'S,
00140 REM* L=# PARAMETERS IN FIT EQN.,P=PHI DATA? =
00150 REM* P=0 NO(NOT PHI BUT ISOPIESTIC MOLALITIES: M1(REF.),M2) P=1,
00160 REM* IF DATA ARE IN  FORM: M,PHI .
00170 DIM M1(300),M2(300),P1(300),P2(300),P3(300),G1(300),G2(300),G3(300)
00180 DIM D2(300),D4(300),D5(300),Y(300),X(300),W(300)
00190 DIM P9(300)
00200 FOR I=1TO 10
00210 READ R(I),Q(I),T(I)
00220 NEXT I
00230 FOR I=1TO8
00240  READ P$(I)
00250 NEXT I
00260 A=.51084
00270 A4=A*(LOG(10))
00280 PRINT
00290 PRINT" TITLE:"INPUT B$
00300 PRINT
00310 PRINT" ENTER: CHARGE(Z+),#PHI,#GAMMA,#PARAMETERS,#REITERATIONS,"
00320 INPUT U,N1,N2,L,S
00330 LET N=N1+N2
00340 PRINT
00350 PRINT
00360 IF N1=0 THEN 00500
00370 REM; INPUT M, PHI FROM DATA FILE (TAPE3)
00380 FOR I=1 TO N1
00390 LET W(I)=1
00400 INPUT FILE(TAPE3) M2(I),P2(I)
00410 NEXT I
00420 PRINT B$
00430 PRINT
00440 PRINT
00450 PRINT "  M", " PHI"
00460 FOR I=1TO N1
00470 PRINT M2(I), P2(I)
00480 NEXT I
00490 PRINT
00500 IF N2=0 THEN 00630
00510 REM; INPUT  M,GAMMA  FROM INPUT FILE (TAPE4)
00520 FORI=N1+1 TO N
00530 INPUT FILE(TAPE4) M2(I),G2(I)
00540 W(I)=1
00550 NEXT I
00560 PRINT B$
00570 PRINT
```

```
00580 PRINT
00590 PRINT "  M"," GAMMA"
00600 FORI=N1+1 TO N
00610 PRINT M2(I),G2(I)
00620 NEXT I
00630 PRINT
00640 FOR I=1TO8
00650 READ A2(I)
00660 NEXT I
00670 READ T$
00680 IF "TEST"=T$ THEN 00720
00690 PRINT" YOU MADE A BOO-BOO IN THE DATA INPUT STATEMENTS"
00700 STOP
00710 REM: CALCULATION OF VARIOUS TERMS OF EQN
00720 FOR I=1TO N
00730 D2(I)=SQR(M2(I)*R(U))
00740 NEXT I
00750 A3=A4*Q(U)
00760 A5=A*Q(U)
00770 V=0
00780FORI=1TON
00790D4(I)=1+A2(1)*D2(I)
00800D5(I)=D4(I)-2*LOG(D4(I))-1/D4(I)
00810 NEXTI
00820 FOR I=1 TO N1
00830 Y(I)=1-A3*D5(I)/(A2(1)↑3*M2(I)*R(U))
00840FORJ=2TOL
00850 Y(I)=Y(I)+A2(J)*M2(I)↑(J-1)*(J-1)/J
00860NEXTJ
00870X(I)=P2(I)-Y(I)
00880V=V+X(I)↑2
00890NEXTI
00900 FORI=N1+1 TO N
00910 Y(I)=-A3*D2(I)/D4(I)
00920 FOR J=2TOL
00930 Y(I)= Y(I)+A2(J)*M2(I)↑(J-1)
00940 NEXT J
00950 X(I)=LOG(G2(I))-Y(I)
00960 V=V+X(I)↑2
00970 NEXT I
00980  V2=V
00990 V=V/(N-L)
01000 V1=SQR(V)
01010 IFS=<0 THEN 01500
01020 PRINT
01030 REM: A2(I) ARE NEW PARAMETERS FOR FITTING EQN
01040FORI=1TOL
01050PRINTA2(I),
01060NEXTI
01070PRINT
01080 PRINT V,V1
01090PRINT
01100S=S-1
01110 REM: MATRIX CALCULATIONS FOR FIT
01120MATZ=ZER(L-1,L-1)
01130MATH=ZER(L-1,L-1)
01140MATB=ZER(L-1)
01150MATG=ZER(L-1)
```

List 10 cont.

```
01160 FOR I=1TO N1
01170 F(1)=3*A3*D5(I)/(A2(1)↑4*M2(I)*R(U))-A3*D2(I)/(A2(1)*D4(I)↑2)
01180FORJ=2TOL
01190F(J)=(J-1)*M2(I)↑(J-1)/J
01200 NEXT J
01210 GOSUB 01310
01220 NEXT I
01230 FORI=N1+1 TO N
01240F(1)=A3*D2(I)↑2/D4(I)↑2
01250 FOR J=2 TO L
01260 F(J)=M2(I)↑(J-1)
01270 NEXT J
01280 GOSUB 01310
01290GO TO 01380
01300 REM: SUBROUTINE FOR CALCULATING NEW CONSTANTS OF FIT EQN
01310FORJ=0TOL-1
01320FORK=JTOL-1
01330H(J,K)=H(J,K)+F(J+1)*F(K+1)*W(I)
01340NEXTK
01350G(J)=G(J)+X(I)*F(J+1)*W(I)
01360NEXTJ
01370 RETURN
01380NEXTI
01390FORJ=1TOL-1
01400FORK=0TOJ-1
01410H(J,K)=H(K,J)
01420NEXTK
01430NEXTJ
01440MATZ=INV(H)
01450MATB=Z*G
01460FORI=1TOL
01470A2(I)=A2(I)+B(I-1)
01480NEXTI
01490 GO TO 00770
01500FORI=1TON
01510 G1(I)=-A3*D2(I)/D4(I)
01520FORJ=2TOL
01530G1(I)=G1(I)+A2(J)*M2(I)↑(J-1)
01540NEXTJ
01550 G3(I)=EXP(G1(I))
01560 P3(I)=A-A3*D5(I)/A2(1)↑3/M2(I)/R(U)
01570 FOR J=2TO L
01580 P3(I)=P3(I)+A2(J)*M2(I)↑(J-1)*(J-1)/J
01590 NEXT J
01600NEXTI
01610 FOR I=1 TO L
01620 E1(I)=V*Z(I-1,I-1)
01630 E(I)=SQR(E1(I))
01640 NEXT I
01650PRINT
01660 PRINT
01670 PRINT
01680 REM: OUTPUT FORMATTING AND PRINTING
01690 PRINT"STD DEV Y(OBSVD)          Y=LN(GAMMA) AND/OR PHI"
01700 PRINT V1
```

List 10 cont.

```
01710 PRINT
01720 PRINT"PARAMETER","STD DEV."
01730 FOR I=1 TO L
01740 PRINT P$(I)" ";A2(I),E(I)
01750 NEXT I
01760 PRINT
01770PRINT
01780 IF N2>0 THEN 01810
01790 PRINT B$
01800 PRINT
01810 PRINT
01820 IF N1=0 THEN 01910
01830 PRINT"   MOLALITY"," Y= PHI","DEL PHI"
01840 REM: PROVISION IS MADE FOR SAVING AN OUTPUT FILE "TAPE1" WHICH
01850 REM:    CONTAINS M AND DELTA PHI (EXP-CALC.)
01860 FOR I=1 TO N1
01870 PRINT FILE(TAPE1) USING 02000, M2(I);X(I)
01880 PRINT USING 01890, M2(I),Y(I),X(I)
01890 : ###.######   -##.######     -##.####
01900 NEXT I
01910 PRINT
01920 IF N2=0 THEN 02030
01930 PRINT"    MOLALITY","Y= LN(GAMMA)","DEL LN(GAMMA)","   GAMMA","DEL GAMMA"
01940 REM: PROVISION FOR SAVING AN OUTPUT FILE "TAPE2" WHICH
01950 REM:    CONTAINS M AND DELTA GAMMA (EXP-CALC.)
01960 FORI=N1+1 TO N
01970 PRINT FILE(TAPE2) USING 02000,M2(I);G3(I)-G2(I)
01980 PRINT USING 02010,M2(I),Y(I),X(I),G3(I),G2(I)-G3(I)
01990 NEXT I
02000 :  ###.###### -#.#####
02010 : -###.######   -##.######     -##.#####     -###.#####     -##.####
02020 REM:  OUTPUT FORMATS ARE SPECIFIED BY LINE BEGINNING WITH  " : ".
02030 PRINT
02040 REM: 1ST DATA IS PROPER FACTORS FOR IONIC STRENGH CALCULATIONS
02050 REM* NEXT ARE INITIAL PARAMETERS, FOLLOWED BY "TEST" TO INSURE
02060 REM:         PROPER INPUT FORMATS HAVE BEEN FOLLOWED.
02070DATA1,1,2,3,2,3,6,3,4,10,4,5,4,4,2,15,6,5,12,8,3,9,9,2,42,12,7,16,16,2
02080 DATA B,C,D,E,F,G,H,I
02090 DATA 1.5,1,1,1,0,0,0,0
02100 DATA"TEST"
02110 END
```

List 11

```
GET,TAPE3=FINPHI1
READY.


GET,TAPE4=FINGAM1
READY.


RUN

 76/05/05. 13.41.22.
PROGRAM    EVALU


 TITLE: ?  CACL2   PARTIAL DATA FIT FOR EXAMPLE.

 ENTER: CHARGE(Z+),#PHI,#GAMMA,#PARAMETERS,#REITERATIONS,
? 2, 10,10, 5, 3


CACL2   PARTIAL DATA FIT FOR EXAMPLE.


 M             PHI
 .25           .88465
 2             1.38866
 2.5           1.58271
 3             1.77477
 3.5           1.9981
 4             2.18362
 4.5           2.38549
 5             2.57681
 6             2.89981
 1.985         1.38869

CACL2   PARTIAL DATA FIT FOR EXAMPLE.


 M             GAMMA
 .03504        .604364
 .06294        .558764
 .1032         .523894
 .0435         .588386
 .0628         .5565
 .0781         .552901
 .002          .847781
 .005          .784028
 .01           .723185
 .02           .656759


 1.5           1              1              1              0

 4032.95       63.5055


 1.59738       .369807        6.93341E-2     -9.86412E-4    -5.80757E-4

 1.00885E-4    1.00442E-2
```

List 11 cont.

```
 1.59788         .373576         6.76287E-2     -6.47017E-4    -6.04453E-4

 1.00327E-4      1.00163E-2



STD DEV Y(OBSVD)             Y=LN(GAMMA) AND/OR PHI
 1.00163E-2

PARAMETER       STD DEV.
B  1.59787       4.20983E-2
C  .373585       7.20164E-2
D  6.76236E-2    4.10491E-2
E -6.45916E-4    9.08279E-3
F -6.04533E-4    6.77734E-4


   MOLALITY      Y= PHI         DEL PHI
    .250000       .875046         .0096
   2.000000      1.395613        -.0070
   2.500000      1.581887         .0008
   3.000000      1.778835        -.0041
   3.500000      1.982316         .0158
   4.000000      2.187403        -.0038
   4.500000      2.388399        -.0029
   5.000000      2.578858        -.0020
   6.000000      2.898649         .0012
   1.985000      1.390226        -.0015

    MOLALITY    Y= LN(GAMMA)    DEL LN(GAMMA)      GAMMA        DEL GAMMA
     .035040     -.489265         -.01431          .61308        -.00871
     .062940     -.579552         -.00248          .56015        -.00139
     .103200     -.653642          .00718          .52015         .00375
     .043500     -.522439         -.00793          .59307        -.00469
     .062800     -.579209         -.00688          .56034        -.00384
     .078100     -.612507          .01993          .54199         .01091
     .002000     -.161407         -.00373          .85095        -.00316
     .005000     -.239096         -.00421          .78734        -.00331
     .010000     -.315398         -.00869          .72950        -.00631
     .020000     -.406649         -.01379          .66588        -.00912


SS        1.660 SECS.

RUN COMPLETE.
```

8. Calculation of Tables of Phi and Gamma at Rounded Molalities

8.1a. Program: GAMPHI

General Description

The program GAMPHI, using the constants obtained for the fitting equation in the evaluation procedure eq (11), calculates values for the mean activity coefficient, the osmotic coefficient, the activity of the solvent (H_2O) and the excess Gibbs energy at specified molalities or prints a table at rounded molalities up to a maximum molality specified by the user. The program is primarily a conversational program, where the user is asked questions during the run, which directs the pathway and output of the program.

The data inputs may all be easily converted to internal read statements, if the conversational mode is not desired.

In all cases of input questions, a typed-in "YES" is a positive input and anything else is assumed to be negative. If the input asked for is a number, then a number must be entered, even if zero (e.g. the number of points in a file and the maximum molality in the table). Choices are made for the following courses of action, listed in the order of their appearance in the program:

a. Charge type?

b. Single molality? 'YES' or 'NO'

c. Use data listed at line no. 1300? Input 'YES' or 'NO'

d. Input data from a file? Input 'YES' or 'NO'

  (1) If so - enter number of data points. Input N

If none of the three choices are specified, the user is asked to input the maximum molality for the table to be printed.

A table is printed from 0 to the maximum molality at (a) 0.001. $\text{mol}\cdot\text{kg}^{-1}$ intervals to 0.1 $\text{mol}\cdot\text{kg}^{-1}$, then at (b) 0.01 $\text{mol}\cdot\text{kg}^{-1}$ intervals to 0.1 mol•kg^{-1}, at (c) 0.1 mol•kg^{-1} intervals to 2.0 mol•kg^{-1}, and at (d) every 0.5 mol•kg^{-1} intervals thereafter. The program is listed as list 12 and sample outputs are illustrated in lists 13, 14, 15, and 16.

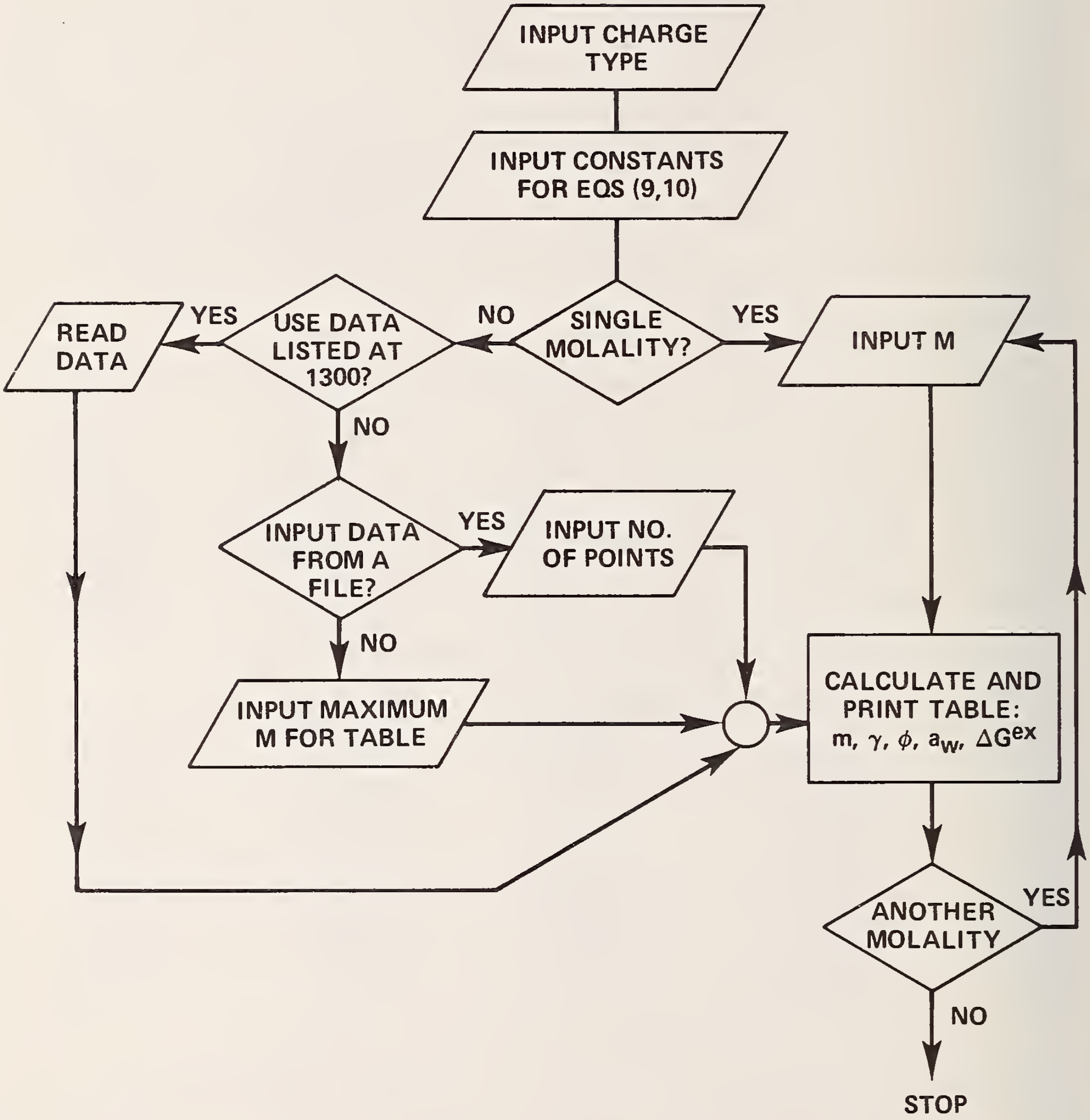

Fig. 6. Flow Diagram for : 'GAMPHI'.

List 12

```
LIST

 76/05/05. 09.37.11.
PROGRAM    GAMPHI

00100 REM* BRS VERSION 2-26-75.  CALCULATES GAMMA AND PHI AT
00110 REM*SELECTED MOLALITIES OR PRINTS TABLE.
00120 REM: MODIFIED 10-2-75.
00130 REM: ENTER (8) CONSTANTS FOR HAMER-WU MODIF. EQN. AT LINE NO. 1200
00140 REM: INPUT DATA: SET OF MOLALITIES;
00150 REM: OUTPUT:   M, GAMMA, PHI, ACTIVITY (H2O), EXCESS GIBBS ENERGY
00160 DIM G2(200),G9(200),A7(200),A9(200)
00170 DIM X(200),G(200),P(200),G1(200)
00180READA,B
00190FORI=1TO10
00200READ Y(I),Z(I),W(I)
00210NEXTI
00220 PRINT"CHARGE TYPE (LIST LINE NO. 1160 FOR EXPLANATION) =" INPUT V
00230 PRINT"SINGLE M" INPUT T$
00240 PRINT
00250 PRINT" USE SET OF MOLALITIES ENTERED AT LINE NO. 1300" INPUT S$
00260 IF "YES"=S$ THEN 00300
00270 PRINT " INPUT MOLALITIES FROM FILE" INPUT R$
00280 IF "YES"=R$ THEN 00300
00290 GOTO 00310
00300 PRINT" NO. OF POINTS" INPUT N
00310FORI=1TO8
00320READC(I)
00330NEXTI
00340 PRINT
00350 PRINT
00360 PRINT" CONSTANTS USED:"C(1);C(2);C(3);C(4);C(5);C(6);C(7);C(8)
00370 PRINT
00380 LET A=A*SQR(Y(V))
00390 LET C(1)=C(1)*SQR(Y(V))
00400 IF "YES"=R$ THEN 00660
00410 IF "YES"=T$ THEN 00630
00420 IF "YES"=S$ THEN 00660
00430 PRINT
00440 PRINT"MAXIMUM MOLALITY REQUIRED IN TABLE =" INPUT T
00450 PRINT
00460 PRINT
00470 PRINT" **********"
00480 N= 2*(T-2)+30
00490LETX(1)=.001
00500 FOR I=2 TO 10
00510 X(I)=X(I-1)+.001
00520 NEXT I
00530 FOR I= 11 TO 19
00540 X(I)=X(I-1)+.01
00550 NEXT I
00560 FOR I=20 TO 28
00570 X(I)=X(I-1)+.1
00580NEXTI
00590 FOR I=29 TO N
00600LETX(I)=X(I-1)+.5
00610NEXTI
00620 GO TO 00660
00630 PRINT
```

List 12 cont.

```
00640 PRINT" M ="  INPUT X(1)
00650LETN=1                          [redacted]
00660FORI=1TON
00670 IF "YES"=R$ THEN 00700
00680 IF "YES"=S$ THEN 00720
00690 GO TO 00730
00700 INPUT FILE(TAPE1) X(I)
00710 GO TO 00730
00720 READ X(I)
00730 LET M=X(I)
00740LETQ=SQR(M)
00750LETD=1+C(1)*Q
760 G1(I)=-(LOG(10))*Z(V)*A*Q/D
765 FOR J=2 TO 8
770 G1(I)=G1(I)+(LOG(10))*C(J)*M↑(J-1)
775 NEXT J
00780 LET G(I)=EXP(G1(I))
00790LET G2(I)=1. + G1(I)
00800LETL=LOG(D)
00810LETP(I)=1-2.302585*(Z(V)*A/C(1)↑3/M*(D-2*L-1/D))
815 FOR J=2 TO 8
820 P(I)=P(I)+(LOG(10))*C(J)*M↑(J-1)*(J-1)/J
825 NEXT J
00850 A9(I)=P(I)*W(V)*M/55.5081
00860 A9(I)=EXP(-A9(I))
00870 G9(I)=W(V)*X(I)*8.31441*298.15*(1-P(I)+LOG(G(I)))
00880 NEXT I
00890PRINT
00900 IF "YES"=C$ THEN 00950
00910 PRINT
00920 PRINT
00930 PRINT" MOLALITY";"     GAMMA";"          PHI";"       A (H20)";" DEL. G(EX)"
00940 PRINT
00950 FOR I=1 TO N
00960 IF X(I)>8 THEN 01000
00970 IF X(I)>3 THEN 01020
00980 PRINT USING 01130, X(I),G(I),P(I),A9(I),G9(I)
00990 GOTO 01030
01000 PRINT USING 01150, X(I),G(I),P(I),A9(I),G9(I)
01010 GO TO 01030
01020 PRINT USING 01140, X(I),G(I),P(I),A9(I),G9(I)
01030 PRINT FILE(TAPE2) X(I);G(I);P(I);G9(I)
01040 NEXT I
01050 PRINT
01060 PRINT
01070 PRINT"ANOTHER M" INPUT C$
01080 IF "YES"=C$ THEN 00630
01090 DATA .51084,.32866
01100DATA 1,1,2,3,2,3,6,3,4,10,4,5,4,4,2,15,6,5,12,8,3,9,9,2,42,12,7,16, 16,2
01130 : ##.###      ##.####      ##.####      #.######      -######.
01140 : ##.###      ##.###       ##.####      #.####        -######.
01150 : ##.###     ###.##        ##.###       #.####        -######.
1200 DATA 1.4495, 2.0442E-2, 5.7927E-3, -2.886E-4
1210 DATA 0,0,0,0
1290 REM: START SET OF MOLALITIES AT LINE NO. 1300 -- IF DESIRED.
1295 REM: DATA HERE FOR NACL  3-2-76.
09999 END
```

List 13

```
RUN

 76/05/05. 09.47.09.
PROGRAM   GAMPHI

CHARGE TYPE (SEE TABLE 1 IN TEXT) = ? 1
SINGLE M? YES

 USE SET OF MOLALITIES ENTERED AT LINE NO. 1300 ? NO
 INPUT MOLALITIES FROM FILE ? NO


 CONSTANTS USED: 1.4495  .020442  5.79270E-3 -2.88600E-4  0  0  0  0


 M =?  1.23456


 MOLALITY    GAMMA        PHI      A (H20)       DEL G(EX)

  1.235      .6548       .9452      .958827       -2256.

ANOTHER M ? NO

SS       0.517 SECS.

RUN COMPLETE.
```

List 14

```
ANOTHER EXAMPLE


1300 DATA 1.1,2.1,3.5,6.04

RUN

 76/05/05. 09.54.56.
PROGRAM   GAMPHI

CHARGE TYPE (SEE TABLE 1 IN TEXT) = ? 1
SINGLE M? NO

 USE SET OF MOLALITIES ENTERED AT LINE NO. 1300 ? YES
 NO. OF POINTS? 4


 CONSTANTS USED: 1.4495  .020442  5.79270E-3 -2.88600E-4  0  0  0  0



 MOLALITY     GAMMA        PHI        A (H20)       DEL G(EX)

  1.100       .6554        .9395       .963448       -1974.
  2.100       .6715        .9893       .927876       -4035.
  3.500       .746        1.0795       .8727         -6468.
  6.040       .991        1.2731       .7580         -8453.

ANOTHER M ? NO

SS       0.535 SECS.

RUN COMPLETE.
```

List 15

```
THIS IS ANOTHER EXAMPLE:



RUN

 76/05/05. 09.49.20.
PROGRAM    GAMPHI

CHARGE TYPE (SEE TABLE 1 IN TEXT) = ? 1
SINGLE M? NO

 USE SET OF MOLALITIES ENTERED AT LINE NO. 1300 ? NO
 INPUT MOLALITIES FROM FILE ? NO


 CONSTANTS USED: 1.4495  .020442  5.79270E-3 -2.88600E-4  0  0  0  0


MAXIMUM MOLALITY REQUIRED IN TABLE =? 0.10


 **********


 MOLALITY      GAMMA        PHI       A (H20)       DEL G(EX)

    .001       .9651       .9884      .999964          -0.
    .002       .9519       .9841      .999929          -0.
    .003       .9422       .9809      .999894          -1.
    .004       .9343       .9784      .999859          -1.
    .005       .9276       .9762      .999824          -1.
    .006       .9216       .9743      .999789          -2.
    .007       .9163       .9726      .999755          -2.
    .008       .9114       .9710      .999720          -3.
    .009       .9069       .9696      .999686          -3.
    .010       .9028       .9683      .999651          -3.
    .020       .8719       .9587      .999309          -9.
    .030       .8509       .9524      .998971         -17.
    .040       .8349       .9477      .998635         -25.
    .050       .8218       .9440      .998301         -35.
    .060       .8108       .9410      .997968         -45.
    .070       .8013       .9384      .997636         -56.
    .080       .7929       .9363      .997305         -67.
    .090       .7854       .9344      .996974         -79.
    .100       .7786       .9328      .996645         -91.
    .200       .7340       .9237      .993366        -231.
    .300       .7090       .9207      .990097        -393.
    .400       .6927       .9203      .986824        -570.
    .500       .6812       .9212      .983541        -757.
    .600       .6728       .9231      .980242        -950.
    .700       .6666       .9256      .976926       -1149.
    .800       .6621       .9285      .973590       -1352.

ANOTHER M ? N0


SS        1.043 SECS.

RUN COMPLETE.
```

List 16

```
NEW
FILE NAME:  DATASPL
READY.

TEXT
ENTER TEXT MODE.

1.1
2.3
5.5
6.0
7, .123, .001


EXIT TEXT MODE.

SAVE *DEL*

NOSORT
READY.

SAVE
READY.

OLD
FILE NAME:  GAMPHI
READY.


GET,TAPE1=DATASPL
READY.


RUN

 76/05/05. 09.59.10.
PROGRAM   GAMPHI

CHARGE TYPE (SEE TABLE 1 IN TEXT) = ? 1
SINGLE M? NO

 USE SET OF MOLALITIES ENTERED AT LINE NO. 1300 ? NO
 INPUT MOLALITIES FROM FILE ? YES
 NO. OF POINTS? 7


 CONSTANTS USED: 1.4495  .020442  5.79270E-3 -2.88600E-4  0   0   0   0



 MOLALITY      GAMMA        PHI       A (H20)        DEL G(EX)

  1.100        .6554       .9395      .963448         -1974.
  2.300        .6791      1.0010      .920394         -4425.
  5.500        .928       1.2306      .7836           -8339.
  6.000        .986       1.2700      .7599           -8451.
  7.000       1.118       1.3480      .7118           -8210.
   .123        .7653       .9297      .995888          -120.
   .001        .9651       .9884      .999964            -0.


ANOTHER M ? NO


SS       0.684 SECS.

RUN COMPLETE.
```

9. Summary

This technical note describes tested programs which are suitable for the reduction of experimental data to calculate ϕ and γ from the four methods presented. A non-linear least squares program has been detailed as a correlating function and tables of m, ϕ, γ, a_w, and ΔG^{ex} can be produced using this correlating equation.

The authors invite comments concerning these programs and their use. We solicit programs written by others and are interested in other methods of calculation and testing equations for examining electrolyte data.

Future publications will describe such programs as those used for the calculation of ϕ from freezing point data, as well as for other thermodynamic quantities, such as heats of dilution, solution, equilibrium constants, and other quantities, from various experimental methods.

10. References

[1] Cohen, E. R., and Taylor, B. N., J. Phys. Chem. Reference Data, 2, 663 (1973).

[2] Staples, B. R., and Nuttall, R. L., J. Phys. Chem. Reference Data, 6, xxx (1977), in press.

[3] Stimson, H. F., J. Res. Nat. Bur. Stand., 73A, 493 (1969).

[4] Keenan, J. H., Keyes, F. G., Hill, P. G., and Moore, J. G., "Steam Tables", Int'l Ed. - Metric Units, John Wiley & Sons, Inc., New York (1969) p. 148.

[5] Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," 3rd ed., Butterworth and Co., London, (5th impression, 1970).

FEDERAL INFORMATION PROCESSING STANDARD SOFTWARE SUMMARY

01. Summary date

Yr.	Mo.	Day
76	07	15

02. Summary prepared by (Name and Phone)
Dr. Bert R. Staples (301) 921-3632

03. Summary action
New ☒ Replacement ☐ Deletion ☐
Previous Internal Software ID

04. Software date

Yr.	Mo.	Day
76	05	01

05. Software title
COMPUTER PROGRAMS FOR THE EVALUATION OF ACTIVITY AND OSMOTIC COEFFICIENTS

06. Short title

07. Internal Software ID

08. Software type
☐ Automated Data System
☒ Computer Program
☐ Subroutine/Module

09. Processing mode
☐ Interactive
☐ Batch
☒ Combination

10. Application area
General
☐ Computer Systems Support/Utility
☒ Scientific/Engineering
☐ Bibliographic/Textual
☐ Management/Business
☐ Process Control
☐ Other

Specific
Evaluation of properties of electrolyte solutions

11. Submitting organization and address
316.05
Physical Chemistry Division
National Bureau of Standards
Washington, DC 20234

12. Technical contact(s) and phone
Bert R. Staples (301) 921-3632
Ralph L. Nuttall (301) 921-2765

13. Narrative A number of specialized computer programs have been developed for the purposes of calculating thermodynamic properties directly from experimental data and for subsequent data manipulation, including non-linear least-squares fitting of the data to empirical or semi-empirical equations that describe the function over a range of compositions, temperatures or other parameters. The details of the programs used in the critical evaluation of mean activity and osmotic coefficients and sample runs for each program are discussed. Osmotic coefficients can be calculated from direct vapor pressure measurements or from isopiestic molalities. Activity coefficients can be calculated from electromotive force measurements of galvanic cells, both without liquid-junction and with transference. A non-linear least-squares program fits data from all sources as a function of ϕ and ln γ. Once the parameters of the fitting equation have been obtained, another program can be used to calculate a table of m, γ, ϕ, a_w, and ΔG^{ex} at rounded molalities.

14. Keywords Activity coefficients; aqueous; computer programs; data evaluation; electrolytes; electromotive force; isopiestic method; osmotic coefficients; non-linear least squares; thermodynamic properties; vapor pressure

15. Computer manuf'r and model CDC 6000-series	16. Computer operating system KRONOS 2.1.1	17. Programing language(s) BASIC	18. Number of source program statements 900
19. Computer memory requirements Minimal	20. Tape drives N/A	21. Disk/Drum units N/A	22. Terminals One

23. Other operational requirements
Data file

24. Software availability
Available ☐ Limited ☒ In-house only ☐

25. Documentation availability
Available ☒ Inadequate ☐ In-house only ☐

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5. Publication Date
December 1976

6. Performing Organization Code

7. AUTHOR(S) Bert R. Staples and Ralph L. Nuttall

8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

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WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.
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11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address *(Street, City, State, ZIP)*

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Washington, D. C. 20234

13. Type of Report & Period Covered
Final

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A number of specialized computer programs have been developed for the purposes of calculating thermodynamic properties directly from experimental data and for subsequent data manipulation, including non-linear least-squares fitting of the data to empirical or semi-empirical equations that describe the function over a range of compositions, temperatures or other parameters. The details of the programs used in the critical evaluation of mean activity and osmotic coefficients and sample runs for each program are discussed. Osmotic coefficients can be calculated from direct vapor pressure measurements or from isopiestic molalities. Activity coefficients can be calculated from electromotive force measurements of galvanic cells, both without liquid-junction and with transference. A non-linear least-squares program fits data from all sources as a function of ϕ and ln γ. Once the parameters of the fitting equation have been obtained, another program can be used to calculate a table of m, γ, ϕ, a_w, and ΔG^{ex} at rounded molalities.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Activity coefficients; aqueous; computer programs; data evaluation; electrolytes; electromotive force; isopiestic method; osmotic coefficients non-linear least squares; thermodynamic properties; vapor pressure

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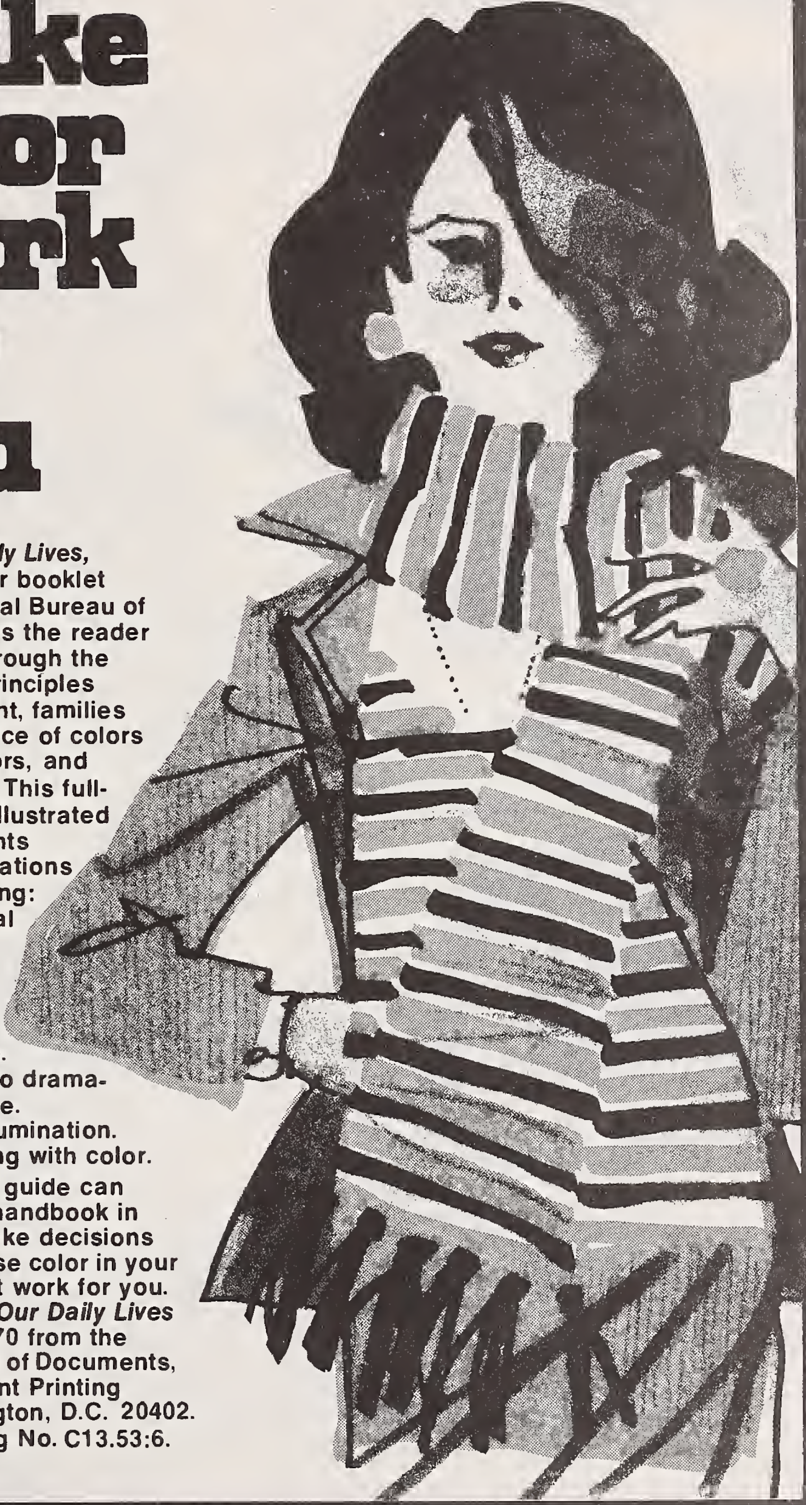

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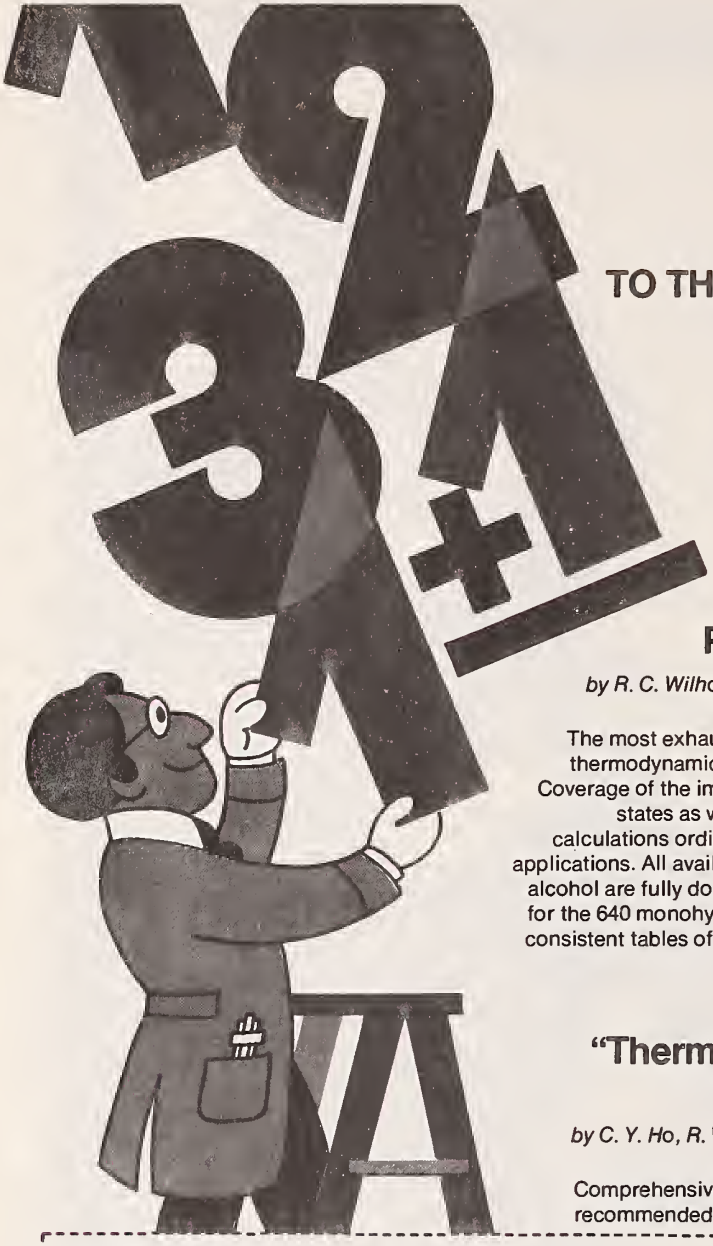

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